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Molecular association studies of 1-propanol in cyclohexane with benzene

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Abstract The molecular association behaviour of 1-propanol in cyclohexane with benzene at various mole fractions has been studied at 303, 308 and 313K. The variation of ultrasonic velocity with the mole fraction of 1-propanol suggests the specific interactions between unlike molecules and also leads to the possibility of temporary dipole or dispersion type interaction among them. The results obtained from the derived acoustical parameters and their excess values clearly reveal the weak interactions present in the system.

Keywords · Dispersion forces, weak interaction, acoustical parameters

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The ultrasonic velocity of a liquid is fundamentally related to the binding forces between the atoms or the molecules. In recent years, the measurements of ultrasonic velocity have been adequately employed in understanding the nature of molecular interaction in ternary mixtures [1-3]. The derived parameters from ultrasonic velocity such as adiabatic compressibility, free volume *etc.* provide a better insight into the molecular environments in liquids [4, 5]. The variation of ultrasonic velocity and related parameters throw much light upon the structural changes associated with the liquid mixtures having weakly interacting components [6-8]. The study of molecular association in organic ternary mixtures having alcohols as one of the components is of particular interest, since alcohol is highly polar and can associate with any other group having some degree of polar attractions. Further, due to higher dipole moment of alcohol, temporary dipoles or induced dipoles can be formed by the inductive effects in the system, which leads to pronounced interactions in the mixture. Owing to these considerations we undertake the present study of molecular association behaviour of 1-propanol in cyclohexane with benzene at 303, 308 and 313K.

The mixtures of various concentrations in mole fractions were prepared by taking purified AR grade samples at 303K. In all the mixtures, the mole fraction of the second component benzene ($x_2 = 0.4$) was kept constant, while the mole fractions of the remaining two components

were varied from 0.1 to 0.5. There is no significance attached to the value of mole fraction at which one of the components was fixed in the mixtures. The only purpose is to have the mixtures of different compositions and so one was fixed and the other two were varied.

The ultrasonic velocities in the pure liquids and liquid mixtures of various concentrations have been measured at 303, 308 and 313K by an ultrasonic interferometer working at 2MHz frequency. The densities and viscosities of the mixtures at the said temperatures are measured using a specific gravity bottle and an Ostwald's viscometer respectively.

The measured ultrasonic velocity (U), density (ρ) and viscosity (η) are used for the computation of the acoustical parameters like adiabatic compressibility (β), free length (L_f), free volume (V_f), internal pressure (π_i) and its excess parameters using the following standard equations :

$$\beta = (U^2\rho)^{-1}, \tag{1}$$

$$L_f = K_T\beta^{1/2}, \tag{2}$$

$$V_f = \left(\frac{MU}{\eta K}\right)^{3/2}, \tag{3}$$

$$\pi_i = bRT\left(\frac{K\eta}{U}\right)^{1/2}\frac{\rho^{2/3}}{M^{7/6}}, \tag{4}$$

$$A^E = A_{\exp} - A_{id}. \tag{5}$$

where the notations have their usual significance.

The values of density, viscosity and velocity at 303, 308 and 313K for the experimental liquids are given in Table 1. The computed acoustical parameters *viz.* adiabatic compressibility, free length, free volume and internal pressure are presented in Table 2. The excess values of these computed parameters are shown in Figure 1 and 2.

Table 1. Values of density (ρ), viscosity (η) and velocity (U)

Mole fraction		ρ Kgm^{-3}			$\eta \times 10^3$ Nsm^{-2}			U ms^{-1}		
		Temperature (K)			Temperature (K)			Temperature (K)		
X_1	X_3	303	308	313	303	308	313	303	308	313
0 0000	0.6000	797.4	792.2	785 4	0 5969	0.5601	0.5258	1222.1	1206.2	1181 8
0 0999	0.4987	799.2	794.4	788.6	0.5904	0.5485	0.5103	1213.4	1191 1	1172.4
0.1990	0.3948	804.4	798.5	791.5	0 5986	0.5651	0.5317	1204.3	1188 8	1165 8
0 2929	0 3151	807.4	802.6	795.8	0 6446	0 6019	0.5479	1201 9	1184 9	1164.1
0.3945	0.1923	813.9	810.3	805.1	0.6772	0.6340	0.5872	1206 2	1186 3	1171.5
0.5087	0.0977	818.2	815.2	808.0	0.7592	0.7039	0.6332	1208.9	1189 7	1173 0
0.5985	0.0000	826.0	823.5	818.9	0.8390	0.7651	0.6929	1215.3	1193 6	1181.9
1.0000	0.0000	795.6	793.4	788.4	1.6344	1.4710	1 2964	1193.0	1180.3	1165.3
0.0000	0.0000	868.1	864.6	856.8	0.5738	0.5271	0.4953	1282.2	1259.5	1244 3
0.0000	1.0000	767.1	762.7	757.8	0.8003	0.7180	0.6673	1230.3	1212.5	1189.1

Table 2. Values of adiabatic compressibility (β), free length (L_f), free volume (V_f) and internal pressure (π_i)

Mole fraction		$\beta \times 10^{10}$ Pa^{-1}			$L_f \times 10^{10}$ m			$V_f \times 10^7$ m^3 mol^{-1}			$\pi_i \times 10^{-6}$ Pa		
		Temperature (K)			Temperature (K)			Temperature (K)			Temperature (K)		
X_1	X_3	303	308	313	303	308	313	303	308	313	303	308	313
0.0000	0.6000	8.3967	8.6776	9 1164	0 5782	0 5925	0 6130	2 4452	2.6377	2.8124	367	363	359
0.0999	0 4987	8.4984	8.8718	9.2255	0.5817	0 5994	0 6166	2 3511	2.5502	2 7788	381	375	369
0.1990	0.3948	8.5715	8.8615	9 2961	0.5842	0 5987	0 6190	2.1740	2 3245	2 4734	403	396	392
0.2929	0.3151	8.5738	8.8744	9 2729	0 5843	0.5992	0 6182	1.8580	2 0157	2 2600	431	425	414
0.3945	0.1923	8.4448	8.7693	9.0504	0.5798	0 5956	0.6108	1 .6459	1.7722	1 9512	462	457	448
0.5087	0.0977	8.3640	8 6668	8.9948	0 5771	0 5921	0 6089	1 3159	1 4390	1.6513	512	504	487
0.5985	0.0000	8.1969	8.5235	8.7419	0.5713	0.5872	0.6003	1 0878	1.2158	1 3900	561	549	531
1.0000	0.0000	8.8307	9.0474	9 3407	0 5929	0 6049	0 6205	0 3281	0 3782	0 4484	881	852	815
0.0000	0.0000	7.0068	7.2910	7.5382	0 5282	0.5431	0.5574	2 6045	2 8800	3.1047	393	385	379
0.0000	1.0000	8.6057	8 9183	9.3327	0 5853	0 6006	0 6202	1 6620	1.8362	2 0741	400	391	381

The perusal of Table 1 reveals that the ultrasonic velocity shows a sudden rise at 0.3 mole fraction of 1- propanol. This behaviour which is different from that of an ideal mixture, can be attributed to inter molecular interactions [9, 10] in the system studied. An exactly reverse trend is observed in the values of adiabatic compressibility (Table 2).

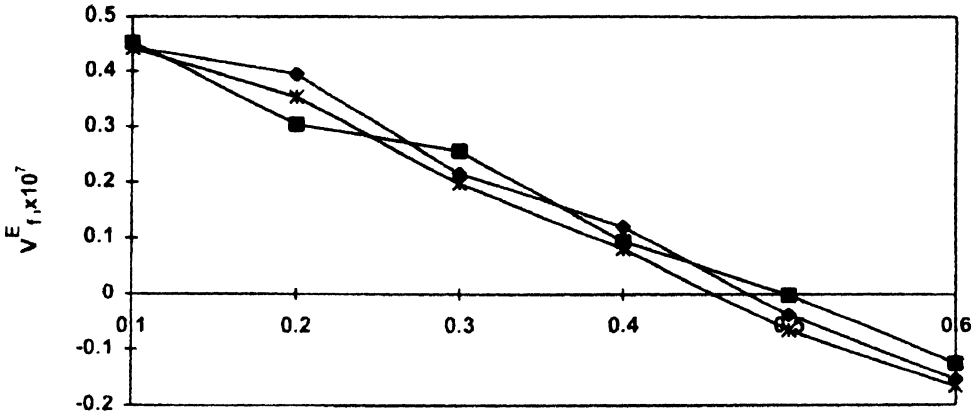

Figure 1. Variation of excess free volume with the mole fraction of 1-propanol

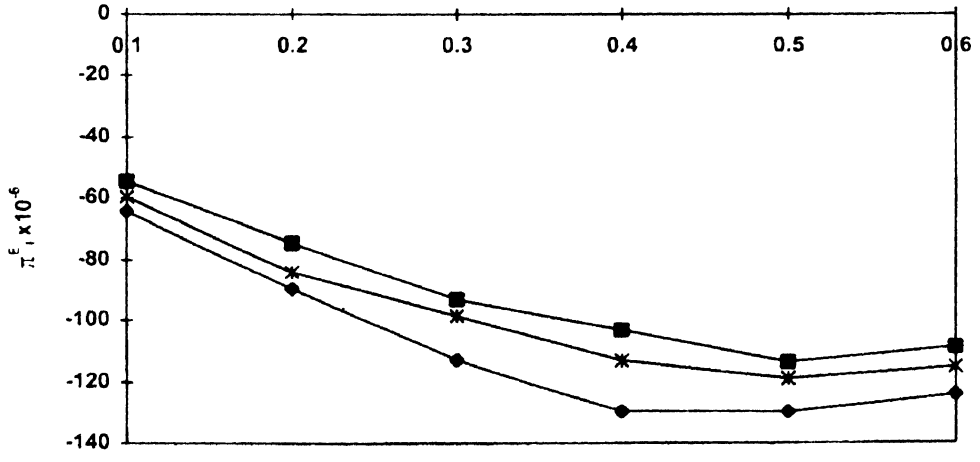

Figure 2. Variation of excess internal pressure with the mole fraction of 1-propanol.

As benzene is having relatively a higher dielectric constant ($\varepsilon = 2.275$) [11] and being an electron donor than cyclohexane ($\varepsilon = 2.02$) [11], the interaction between the molecules of benzene with cyclohexane is found to be weaker than the interactions with the 1-propanol. Since dispersive interactions are dominant between benzene and cyclohexane [12-14], the same type of interaction may also play between the 1-propanol and cyclohexane due to the non-polar nature of cyclohexane and its inertness towards electron donors. The addition of 1-propanol leads to a compact structure due to these dipolar or dispersive type interactions and hence a decrease in free length and compressibility is observed. As this trend is an indicative of clustering together of the molecules [15], the free space between the molecules decrease. However, as the inert solvent (cyclohexane) can break up the *H* bonds in alcohol aggregates [16], the free space can increase. These two opposing effects compensate each

other to different degrees throughout the entire mole fraction range in the system studied. The rise in temperature make the free length and free volume to increase, as expected due to the thermal expansion of the liquid medium [17]. Further, the decrease in free volume and an increase in internal pressure with rise in concentration of 1-propanol, clearly show the increasing magnitude of interactions [18].

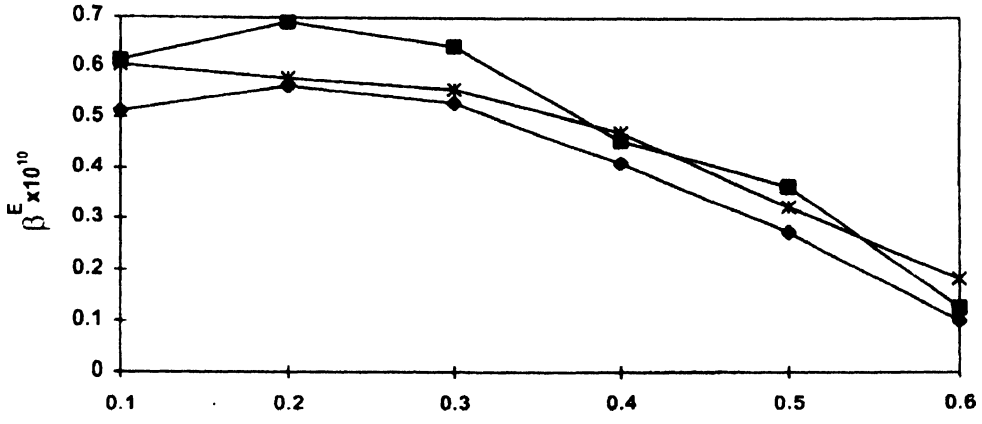

Figure 3. Variation of excess adiabatic compressibility with the mole fraction of 1-propanol

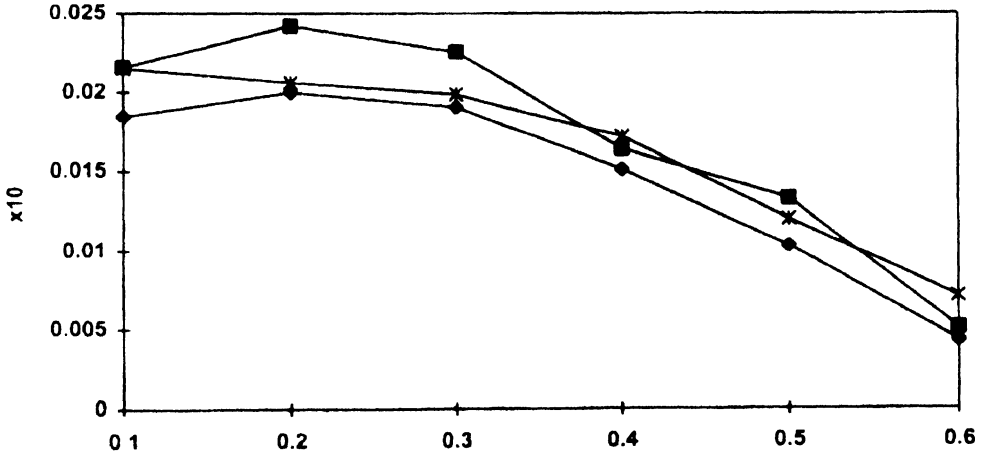

Figure 4. Variation of excess free length with the mole fraction of 1-propanol.

In order to highlight the presence of interaction, the excess values of the respective parameters have been computed and are shown in Figures 1 and 2. The positive sign of excess adiabatic compressibility indicates weak interaction between unlike molecules that results from dispersion forces [19]. Also the trend in excess free length shows specific interactions between the different sizes of molecules [20]. The rise in the values of these parameters with temperature reveals further weakening of interaction. The positive but decreasing nature of excess free volume with increase in concentration of 1-propanol may be attributed to the weakening of dipolar interaction between the molecules of the mixtures. All these observations are in good agreement with Sivanarayana *et al.* [21] and Pal and Bhatti [22]. The negative excess internal pressure in all the mixtures clearly confirms this prediction.

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